

PATENT SPECIFICATION

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(54) METHOD OF TREATING DRINKS USING POWDERED POLYAMIDE ADSORBENTS

- (71) We, AKZO N.V., a body corporate organised under the laws of the Netherlands, of 82 IJssellaan, Arnhem, Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to a method of treating drinks using powdered polyamide adsorbents, more particularly adsorbents based on very fine polyamide powders, optionally mixed with fillers or beer clarifying agents. These adsorbents are excellent for removing polyphenols or proteins and polyphenols from drinks, such as beer, wine or juice.
- It is known that the cloudiness of beer and other drinks at low temperatures, as well as the permanent cloudiness is due to the combination of polyphenols and proteins. The stability of drinks in storage may be substantially improved either by reducing the amount of polyphenols which cause cloudiness or by reducing the amount of high molecular weight protein. The most stable beers, for example, are obtained by reducing the amount of both these major constituents which cause clouding.
- It is known that the substances used for removing the protein component are mainly silicas or silicates used as hydrogels or xerogels. Many methods are known for freeing beer from the polyphenols which cause cloudiness. The adsorbents which have been proposed for this purpose are mainly polyamides.
- Polyphenols belong to the group of tanning agents and for several decades work has been done on the study of the polyamide/tanning system. H. Batzer proposed as far back as 1952 that polyamide powders should be used for the quantitative determination of tanning agents. Chromatographic separation of tanning agents on a polyamide column has also been described (Ber. dtsh. chem. Ges. 90, pages 1125—1128). Quoting from page 1127 of the said report. "The special advantage of this chromatographic system for separating tanning agents and in fact phenolic substances in general, lies in the possibility of separating relative large quantities of substances by a simple method for preparative purposes." The authors of the said report use finest "Perlon" powder, mesh width 200 μ (DIN 30), manufactured by Farwerke Hoechst for their work. ("Perlon" is a Registered Trade Mark.) As will be well-known to those skilled in the art, "Perlon" is a polyamide obtained from ϵ -caprolactom.
- G. Harris and co-workers (published 1959 in J. Inst. Brew. Vol. 65, pages 256—259) made use of the findings of Grossmann and co-workers and used polyamide powder as a selective adsorbent for anthrocyanogens, i.e. polyphenols. In another project (J. Inst. Brew. Vol. 66 1060, page 317) G. Harris and co-workers showed that the adsorbent action of the polyamides depends to a very large extent on their geometrical form. Fine powders or pastes are the most effective. The efficiency is considerably reduced by using fine granulates and drops to zero when tablets and fibre meshes are used.
- The findings of the experts led to several Patents and Patent Applications concerning the stabilisation of beer with polyamides. According to German Patent No. 1,292,612, Perlon powder having a particle diameter of 0.2 mm is used. DOS No. 1,442,339 reports on an apparatus for the physico-chemical stabilisation of beer and similar drinks. Granulated polyamides used as solid bed in a reaction column are proposed for this purpose. According to DOS No. 1,638,866, polyamide chips having an average thickness of from 80 to 100 μ are used, which are pressed to form filter plates, and in DOS. No. 1,442,336 fine polyamide fibres are proposed for clarifying drinks. The fine polyamide fibres, which have a diameter of between 5 and 100 μ , are to be used in the form of filter plates or filter papers or in filter columns.
- In German Patent No. 710,785 it has been

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suggested that hydrated silica as a gel or in a dried form should be used for manufacturing stable beer which will not become cloudy. It is alleged that the adsorbents used for refining and stabilising beer remove undesirable discolouring constituents and unwanted proteins from the beer. In U.S. Patent No. 2,316,241 it is proposed in Example II to use silicas which have been dried at temperatures of up to 300° C, in other words so-called "xerogels", for stabilising beer.

In subsequent years, further Patent Applications were filed for various silicas having a wide variety of properties. The surface of the silica particles varied within the wide range of from 200 to 1000 m²/g and the pore volumes and pore diameters were equally varied. Limits of from 0.35 to 1.8 ml/g and from 30 to 120 Å were claimed for these two properties. According to the Patent literature, almost all silicas in the form of either hydrogels or xerogels which have SiO₂ contents of from 20 to virtually 100% may be used for adsorbing proteins and are all equally suitable for this purpose provided they have been sufficiently size reduced. Not only pure silicas, but also natural and synthetic silicates have been proposed for the adsorption of proteins from beer and other drinks.

All the products mentioned above for stabilising beer have certain disadvantages which are due either to the product itself or to the nature in which it is applied. Silicas and silicates absorb only higher molecular weight proteins. Polyphenols remain practically unadsorbed. The beer therefore remains extremely sensitive to oxygen which favours the formation of polyphenols which in turn cause cloudiness. However, even if atmospheric oxygen is excluded the simpler phenols undergo condensation or polymerisation in the presence of the hydrogen ions in the beer to form polyphenols which give rise to turbidity. The stabilisation of beer with the aid of silica gels or combinations of silica gels and bentonites is generally insufficient for overseas export.

The main disadvantage of using polyamides in powder form is that it becomes too expensive because recovery and regeneration of the polyamide powder is practically impossible to achieve by an economic method. Although the use of polyamide-containing films or chips in a fixed bed process enables the active substance to be regenerated so that the process becomes more economic with regard to the cost of polyamide, this advantage is offset by the following disadvantages:

1) The polyamide-containing films, or polyamide chips, scrapings or fibres are highly active at the beginning of the beer filtration. The adsorbing and stabilising action continuously diminishes proportionately, but not in linear proportion, to the throughput of beer.

- 2) The filtered beer must be thoroughly mixed after filtration in order that a beer with uniform stability may be obtained.
- 3) Regeneration of the filter or fixed bed of polyamide involves time and reagents and requires additional operations which must be carried out extremely carefully to ensure that no traces of sodium hydroxide solution or of the mixture of water and citric acid used as a detergent get into the beer.
- 4) In the course of the washing process, tanning agents are liable to be reprecipitated as the pH falls, and these precipitated tanning agents reduce the capacity of the films or fixed filter bed or contaminate the beer which comes into contact with them.
- 5) The adsorption capacity diminishes with the number of regenerations carried out. This number is therefore limited.

As in all adsorbents, the effective surface area of the silicas and polyamides is an important factor in determining the adsorption activity and capacity. Although there is no difficulty in grinding silicas finely either in the form of xerogels or hydrogels, polyamides are difficult to grind finely on account of their low melting point. Polyamides may be ground finely only by the low temperature-cold grinding process which is very expensive and in any case can only reduce polyamide to powder with particles of from 20 to 400μ. The effective surface of such particles is relatively low. There are other methods available for obtaining fine polymer particles, e.g. having a particle diameter of from 0.1 to 900μ and surfaces of more than 5 m²/g. A method of this type is described in DOS. No. 1,695,038, according to which, for example, polyamides are dissolved in cyclohexanone at elevated temperature under pressure. In a second stage of the process, the solution of polymer is cooled to a temperature at which the polymer precipitates from the solution. The pressure in the vessel must be maintained during the cooling process. After cooling and precipitation the fine powder is separated and purified. This process, however, is expensive and complicated.

It is common knowledge to the expert that, in principle, particles may be converted into coarser and/or purer or finer particles by dissolving them and then reprecipitating them from solution after altering the external conditions of the solution, such as the pressure, temperature and concentration, but this method is generally applicable only to substances which crystallise readily and usually fails when applied to polymers. If, for example, polyamides are dissolved in concentrated sulphuric acid in the conventional manner and the solutions are diluted with water, then thick, uneven threads or soft lumps are obtained which adhere to the stirrer. In some cases the polyamide even forms a slimy substance

which floats to the top where it slowly solidifies in the form of a spongy skin up to several millimetres in thickness.

5 The present invention provides a method of treating a fermented drink which comprises contacting the drink with a powdered poly-
amide adsorbent, the said adsorbent being
10 prepared by a process which comprises dis-
solving a polyamide in from 30 to 55%, by
weight, sulphuric acid, diluting the resulting
solution in order to precipitate the polyamide
to a sulphuric acid concentration of from 10 to
15 26%, by weight, using water or sulphuric acid
which has a concentration of less than 20%,
by weight, such that the proportion, by weight,
of total H_2SO_4 : polyamide is between 14:1
and 4:1 and the proportion of grams of poly-
amide: ml of diluted sulphuric acid at the
end of dilution is between 1:50 and 1:14.

20 The precipitation of the polyamide powders
is preferably carried out in the presence of
inorganic pulverulent fillers which are sub-
stantially acid resistant, such as kieselguhr,
kaolin, silica and clay, or in the presence of
25 beer clarifying agents based on silica or sili-
cates, and the solids are preferably sub-
sequently filtered, washed out and preferably
size reduced, either in the wet state or partly
or completely dried.

30 The polyamide powders used according to
the present invention are extremely fine and
have large surface areas, of for example, more
than 3 m²/g.

35 The polyamides used may be those com-
monly used as textile raw materials, especially
the polyamide of caprolactam.

The preferred conditions employed for pre-
paring the polyamide powder are as follows:

- 40 1) Concentration of the sulphuric acid used
for dissolving the polyamide: from 33 to
38%, by weight;
- 2) Concentration of sulphuric acid at the
end of dilution: from 23 to 25%, by
weight;
- 45 3) Proportion, by weight, of total H_2SO_4 :
polyamide between 10:1 and 5:1;
- 4) Proportion of grams of polyamide: ml of
diluted sulphuric acid at the end of dilution
between 1:35 and 1:18.

50 If, as is preferred, precipitation of the
polyamide powder is carried out in the pre-
sence of fillers or beer clarifying agents, the
latter may be present in quantities of from 10
to 96%, by weight, preferably from 50 to
55 90%, by weight.

The specific surface of the fillers and beer
clarifying agents, determined by the BET
method (see Kittel, Pigments 1960, pages
109—111) should preferably be between 2 and
60 900 m²/g, more preferably between 50 and
800 m²/g.

The fillers and beer clarifying agents are
preferably used in the form of aqueous or

65 sulphuric acid suspensions or sols or as dry
powders. They are added either to the poly-
amide solution or to the water or dilute
sulphuric acid used for solution.

Precipitation is generally carried out at
temperatures of between 10 and 80° C, pre-
70 ferably at room temperature, and with vigorous
stirring.

The fine polyamide powders used according
to the present invention are excellent adsor-
bents for polyphenols and are far superior in
their activity and capacity to known poly-
75 amide powders.

It has now surprisingly been found that
that efficiency of polyamide adsorbents is even
greater if, as is preferred, the precipitation
of the polyamide is carried out in the presence
80 of fillers. If, for example, a mixture of equal
parts, by weight, of polyamide powder and
clay is used, then the adsorption values ob-
tained for polyphenols are equal to or even
higher than those obtained with an equal
85 quantity of commercially obtainable fine, pure
polyamide powder even though the mixture
has only half the polyamide content.

If precipitation of the polyamide powder
is carried out in the presence of beer clarify-
90 ing agents, such as silica or silicates, which are
well known to act as protein adsorbents, then
the products obtained are adsorbents both for
polyphenols and for proteins. This result is
surprising since it would have been assumed
95 that the homogeneous combination of poly-
amide powder and beer clarifying agent would
not be particularly adsorbent either for pro-
teins or for polyphenols because the polyamide
normally has a deleterious influence on protein
100 adsorption while silica normally has a dele-
terious influence on polyphenol adsorption.

The combinations of polyamide powder and
filler are mainly intended for the adsorption
of polyphenols. The fillers may be used in the
105 form of finely divided inorganic products
which are insoluble or only slightly soluble
in sulphuric acid solutions containing up to
55%, by weight, of H_2SO_4 , e.g. silica having
a surface area of less than 200 m²/g, kiesel-
110 guhr, alumina, clay or kaolin. Combinations
of polyamide powder and silica which have
larger surface areas are intended mainly for
the adsorption of both polyphenol and proteins.
Any amorphous precipitated silica and silicates
115 having surface areas of more than 200 m²/g
known under the general name of "beer
clarifying agents" are suitable for this purpose.

The list given above does not restrict the
possibilities of the present invention, but is
120 only intended to explain the terms "fillers"
and "beer clarifying agents".

The invention will now be explained in
greater detail by the following Examples.

Example 1.

(a) Preparation of the polyamide powder.

7.5 g of pulverulent polycaprolactam were

5 dissolved in 60 ml of a 48%, by weight, sulphuric acid at a temperature of 65° C in the course of 30 minutes with stirring. The solution was cooled to about 25° C and slowly introduced into 150 ml of water with stirring. A fine, chalky white precipitate formed, which was suction filtered and washed. The wet filter cake weighed 23.72 g. After careful drying in a vacuum dessicator, the filter cake weighed 7.06 g. The surface area of the powder, determined by the BET method, is 8 m²/g. From this figure, the average particle size of the powder is calculated to be from 0.6 to 0.7 μ , a degree of fineness which cannot be achieved by any grinding process.

(b) *Determination of the adsorption activity.*

500 ml of decarbonated beer were shaken with 250 mg (=50g/Hl) of the polyamide powder described under 1(a) and then filtered. For comparison, the same operation was car-

ried out with a trade product sold as "PERLON-powder for quantitative polyphenol determination". In this product, 39% of the particles were below 40 μ and 16% were below 10 μ (product P 10).

A comparison test was carried out with polyamide powder which was used as starting material for preparing the polyamide powder according to the present invention described under 1(a). In this starting material, 17% of the particles were below 40 μ and 1.5% below 20 μ .

(c) *Polyphenol determination.*

The polyphenol content and residual polyphenol content were determined in a 10 ml sample of stabilised beer and an equal quantity of untreated beer (O-beer) by the method of Harris and Rickets (R. W. J. Inst. Brew 1959 page 331)

TABLE 1

Dosage: 50 g/Hl	O-beer	Contact times			
		3 min.	30 min.	60 min.	4 hours
Polyamide powder					
Example 1(a)					
Polyphenols mg/l	43.74	32.62	29.67	30.02	29.79
Difference from O-beer	—	-11.12	-14.07	-13.72	-13.95
Reduction in %	—	25.40	32.20	31.30	31.95
Product P10					
(Comparison)					
Polyphenols mg/l	35.70	29.40	29.70	27.80	27.30
Difference from O-beer	—	-6.30	-6.00	-7.90	-8.40
Reduction in %	—	17.60	16.80	22.10	23.50
Starting material for Example 1(a)					
(Comparison)					
Polyphenols	45.98	44.42			
Difference from O-beer	—	-1.56			
Reduction in %	—	3.4			

45 The remarkably better adsorption activity of the polyamide powder used according to the present invention is obvious. Saturation is reached after 30 minutes' contact time and the quantity of adsorbed polyphenols is about twice as high as in "P 10" based on the percentage reduction.

Example 2.

70 g of the polyamide used in Example 1(a) were dissolved in 650 ml of 52%, by weight, sulphuric acid at room temperature in the course of 60 minutes. 200 ml of 12.5%, by weight, sulphuric acid were added to 100 g of this polyamide solution with stirring. A very

fine grained precipitate formed in the course of several hours. This precipitate was filtered, washed and dried at 90° C.

Example 3.

- 5 100 g of the solution of polyamide in sulphuric acid prepared in Example 2 were weighed out. This solution was introduced into 185 ml of water and diluted to a final concentration of 17.3%, by weight, of H₂SO₄. A

fine precipitate formed which was worked-up as described in Example 2. 10

The polyamide powders obtained in Examples 2 and 3 were used for the adsorption of polyphenols in beer as explained under 1(b). Another experiment was carried out with a polyamide powder which was similar to that used in Example 1(a) except that it had not been dried completely, but only to a residual water content of about 50%. 15

TABLE 2

3 min. contact time Dosage: 50 g/Hl Dry substance	O-beer	p 10	Product of Example 1		Product of Example 2	Product of Example 3
			Dry	50% H ₂ O(*)		
Polyphenols mg/l 1st determination	32.86	31.32	27.42	27.07	27.30	24.94
2nd determination	33.09	31.09	27.54	27.42	27.07	25.77
Average value	32.97	31.21	27.48	27.24	27.18	25.36
Difference from O-beer	—	-1.76	-5.49	-5.73	-5.79	-7.61
Reduction in %	—	5.34	16.69	17.39	17.58	23.69

(*) The polyamide powder which contained 50% of water was used in a quantity of 94.34 g/Hl, which corresponds to 50 g/Hl of dry substance.

- 25 The experiments show that polyphenol powders prepared according to the present invention absorb 3 to 4 times as much polyphenol as does product "P 10" from the export beer of a German brewery used for the tests.

- 30 The economic advantage of the method according to the present invention depends among other things on keeping the total consumption of sulphuric acid as low as possible and ensuring that after removal of the polyamide powder the diluted sulphuric acid is obtained in a sufficiently high concentration for other purposes. This may be achieved by the following method:

- 35 100 ml of 95%, by weight, sulphuric acid were diluted with 300 ml of water to a concentration of about 36%, by weight. 25 to 40 g of polyamide were dissolved in this diluted acid at room temperature in the course of 30 minutes with stirring. Dilution and precipitation were carried out using 216 ml of water. The final concentration of the sulphuric acid was approximately 25%, by weight.

- 45 42 ml of 95%, by weight, sulphuric acid were added to 358 ml of this 25%, by weight, sulphuric acid. The resulting acid was used for dissolving 25 g of polyamide. A fine polyamide powder having a high adsorption activity is again obtained by adding water until the final sulphuric acid concentration is 25%, by weight. 50 The sulphuric acid content which was lost by washing was from 65 to 75 g of 25%, by

weight, sulphuric acid or on an average about 60 ml of dilute sulphuric acid, which corresponds to 17.5 g of 100%, by weight, sulphuric acid. 200 ml of 25%, by weight, of sulphuric acid become available for other purposes with each repetition of the process. 55

If precipitation of the polyamide powder is carried out in the presence of fillers in proportions of 25 g, the loss due to washing is about twice as much. 60

The following Examples were carried out under the solution and precipitation conditions mentioned above. 65

Example 4.

A solution of 25 g of polyamide in 400 ml of 36%, by weight, sulphuric acid was first prepared at room temperature. This solution was added to 216 ml of water in which 25 g of active silica which had a surface area of 170 m²/g had been suspended. 70

Example 5.

Example 4 was repeated with this difference that the aqueous silica suspension was added to the polyamide solution. 75

The polyamide/silica adsorbents prepared according to Examples 4 and 5 were used for removing polyphenols from beer, employing the same conditions as in the previous experiments. 80

For comparison, polyvinyl pyrrolidone pow-

der (PVP) was used, which is known to have a 2 to 2.5 times greater effect than commercial polyamide powder. This PVP powder, how-

ever, cannot be used for stabilising beer on account of the high proportion of soluble constituents contained in it.

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TABLE 3

3 minutes contact time Dosage: 25 g/Hl	O-beer	PVP powder (for comparison)	Product of Example 4	Product of Example 5
Polyphenols mg/l				
1st determination	35.93	28.84	29.43	29.43
2nd determination	35.93	28.84	29.43	29.79
Average value	35.93	28.84	29.43	29.61
Difference from O-beer	—	-7.09	-6.50	-6.32
Reduction in %	—	19.73	18.09	17.58
Δ mg polyphenols Original weight of substance g/Hl	—	0.284	0.260	0.253
Original weight of polymer g/Hl	—	22.58	10.99	13.37
Δ mg polyphenols Original weight of polymer g/Hl	—	0.314	0.591	0.473
Solids content % 105°C	—	90.43	84.87	97.59
Ash residue %(*)	—	0.117	40.92	44.12

(*) The ash residue is based on the original weight of substance used for absorption.

10 The experiments show that PVP powder and the polyamide/silica products used according to the present invention bind approximately the same quantities of polyphenols, based on the original weight of substance, but
15 when the results are based on the original weight of polymer, the products prepared according to Examples 4 and 5 are found to produce much better results. It is also obvious that the polyamide powder present in combination with silica has 4 to 5 times the activity of a commercial polyamide powder.

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Example 6.

25 g of polyamide were dissolved at room

temperature in accordance with Example 4 and precipitated in the presence of 25 g of kaolin of the type used as brush-on paste in the paper industry.

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Example 7.

25 g of polyamide were dissolved in sulphuric acid at room temperature as described in Example 4. A suspension of 25 g of kieselguhr (trade name "Hyflo Supercel")
30 in 216 ml of water was slowly added to this solution with stirring.

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The products obtained in Examples 6 and 7 were used for the adsorption of polyphenol. The following results were obtained:

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TABLE 4

3 min. contact time Dosage: 25 g/Hl Substance	O-beer	Product P 10	Product Example 6	Product Example 7
Polyphenols mg/l				
1st determination	34.28	28.84	27.42	27.30
2nd determination	34.28	28.96	27.66	27.07
Mean value	34.28	28.90	27.54	27.18
Difference from O-beer	—	-6.44	-6.86	-7.10
Reduction %	—	-18.78	-20.01	-20.71
Δ mg polyphenols				
Dosage of substance g/Hl	—	0.259	0.274	0.284
Original weight of polyamide g/Hl	—	24.16	14.52	12.06
Δ mg polyphenols original polyamide weight g/Hl	—	0.268	0.472	0.588
Solids content % 105°C	—	97.02	98.89	98.89
Ash residue %(*)	—	0.38	40.83	50.66

5 The adsorption values summarised in the
following Table 5 were obtained with combinations of polyamide powder and a beer
clarifying agent which in its original form
is a silica hydrogel having a surface area of
approximately 500 m²/g. In experiments 8 to
10 11, the polyamide powder was dissolved in
sulphuric acid at room temperature and precipitation of the polyamide was carried out
in the presence of the beer clarifying agent
under the conditions specified in Example 4.

- Example 8.
35 g of polyamide + 35 g of silica hydrogel
(40% SiO₂). 15
- Example 9.
25 g of polyamide + 5 g of silica hydrogel
(40% SiO₂).
- Example 10.
25 g of polyamide + 75 g of silica hydrogel
(40% SiO₂). 20
- Example 11.
25 g of polyamide + 200 g of silica hydrogel
(40% SiO₂)

TABLE 5

3 min. contact time Dosage: 25 g/Hl Substance	O-beer	Product P 10	Product Example 8	Product Example 9	Product Example 10	Product Example 11
Polyphenols mg/l						
1st determination	29.55	27.07	25.89	25.64	27.89	25.29
2nd determination	29.43	27.30	25.89	25.89	27.89	25.53
Mean value	29.49	27.19	25.89	25.77	27.89	25.41
Difference from O-beer	—	-2.36	-3.60	-3.72	-1.60	-4.08
Reduction %	—	-8.00	-12.20	-12.61	-5.42	-13.83
Δ mg polyphenols						
Substance dosage g/Hl	—	0.094	0.144	0.149	0.064	0.163
Original polyamide weight g/Hl	—	24.16	17.56	10.39	5.47	4.22
Δ mg polyphenols						
Original polyamide weight g/Hl	—	0.104	0.205	0.358	0.292	0.996
Solids content % 105°C	—	97.02	98.13	54.38	71.94	67.20
Ash residue %(*)	—	0.38	27.88	12.83	50.07	50.34

5 It is known that the activity of beer clarifying agents which remove protein from beer may be determined by the ammonium sulphate test. The larger the quantity of ammonium sulphate solution which may be added to the beer before the cloudiness increases by two EEC units, the more active is the beer clarifying agent. The difference in ml between saturated ammonium sulphate solution and O-beer is a proportional measure for the quantity of protein adsorbed and serves as a comparison

15 for beer clarifying agents based on pure SiO₂ gel. To determine the protein adsorption, the ammonium sulphate test was carried out with the product according to Examples 10 and 11 and with pure, approximately 50% SiO₂ gel which was used for preparing the samples according to Examples 10 and 11. The results are shown in Table 6. It clearly shows the more powerful protein adsorption of the samples according to Examples 10 and 11.

TABLE 6

Dosage 100 g/Hl of product; contact time 3 minutes

	ml of saturated ammonium sulphate solution	Difference from O-beer ml	SiO ₂ %	Activity quotient(*)
O-beer	1.70 ml	—	—	—
Example 10	2.90 ml	1.20	50.07	2.40
Example 11	2.95 ml	1.25	50.34	2.49
SiO ₂ -gel	2.60	0.90	49.00	1.84

(*) Activity quotient at a given dosage = $\frac{\text{ml of saturated ammonium sulphate solution} \times 100}{\% \text{ SiO}_2}$

Being aware of the Food and Drugs Act, 1955, we make no claim herein to the use of the present invention in contravention thereof.

WHAT WE CLAIM IS:—

- 5 1. A method of treating a fermented drink which comprises contacting the drink with a powdered polyamide adsorbent, the said adsorbent being prepared by a process which comprises dissolving a polyamide in from 30 to 55%, by weight, sulphuric acid, diluting the resulting solution in order to precipitate the polyamide to a sulphuric acid concentration of from 10 to 26%, by weight, using water or sulphuric acid which has a concentration of less than 20%, by weight, such that the proportion, by weight, of total H_2SO_4 :polyamide is between 14:1 and 4:1 and the proportion of grams of polyamide:ml of diluted sulphuric acid at the end of dilution is between 1:50 and 1:14.
- 10 2. A method as claimed in claim 1 in which the precipitation of the polyamide is carried out in the presence of acid resistant fillers and/or beer clarifying agents.
- 15 3. A method as claimed in claim 2 in which the filler is kieselguhr, kaolin, silica or alumina.
- 20 4. A method as claimed in claim 2 or claim 3 in which the beer clarifying agent is or contains silica and/or silicates.
- 25 5. A method as claimed in any of claims 1 to 4 in which the precipitated polyamide is filtered, washed and partly or completely dried.
- 30 6. A method as claimed in any of claims 1 to 5 in which the precipitated polyamide is size reduced in either the wet or dry state.
- 35 7. A method as claimed in any of claims 1 to 6 in which the polyamide used in the polyamide of caprolactam.
- 40 8. A method as claimed in any of claims 1 to 7 in which the concentration of the sulphuric acid used for dissolving the polyamide is from 33 to 38%, by weight.
- 45 9. A method as claimed in any of claims 1 to 8 in which the concentration of sulphuric acid at the end of dilution is from 23 to 25%, by weight.
- 50 10. A method as claimed in any of claims 1 to 9 in which the proportion, by weight, of total H_2SO_4 :polyamide is between 10:1 and 5:1.
11. A method as claimed in any of claims 1 to 10 in which the proportion of grams of polyamide:ml of diluted sulphuric acid at the end of dilution is between 1:35 and 1:18. 55
12. A method as claimed in any of claims 2 to 11 in which the polyamide powder is precipitated in the presence of fillers and/or beer clarifying agents, which are present in quantities of from 10 to 96%, by weight. 60
13. A method as claimed in claim 12 in which quantities of from 50 to 90%, by weight, are present.
14. A method as claimed in any of claims 2 to 12 in which the specific surface area of the fillers and beer clarifying agents determined by the BET method is between 2 and 900 m^2/g . 65
15. A method as claimed in claim 14 in which the area is between 50 and 800 m^2/g . 70
16. A method as claimed in any of claims 2 to 15 in which the fillers and beer clarifying agents are used as aqueous or sulphuric acid suspensions or sols or as dry powders.
17. A method as claimed in any of claims 1 to 16 in which the solution and precipitation of the polyamide are carried out at a temperature of between 10 and 80° C. 75
18. A method as claimed in any of claims 1 to 17 in which dilution is carried out slowly with vigorous stirring. 80
19. A method as claimed in any of claims 1 to 18 in which the drink is wine or juice.
20. A method as claimed in any of claims 1 to 18 in which the drink is beer. 85
21. A method as claimed in claim 1 substantially as herein described.
22. A method as claimed in claim 1 substantially as herein described with reference to any one of the Examples. 90
23. Fermented drinks when treated by a method as claimed in any of claims 1 to 22.
24. Beer, wine or juice when treated by a method as claimed in any of claims 1 to 22.

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